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PATENT OFFICE

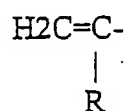
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Aromatic polyethers containing olefinic terminal groups

Polyphenylene ethers containing olefinic, polymerisable terminal groups, and the use of such polyphenylene ethers for the preparation of copolymers with other compounds containing polymerisable double bonds.

Patent claims

1. Polyphenylene ethers, characterised by the fact, that they contain olefinic terminal groups of the general formula



in which R can be hydrogen or an aliphatic alkyl group.

2. Use of the polyphenylene ethers containing olefinic terminal groups for the preparation of copolymers with other compounds containing polymerisable double bonds.

Aromatic polyether with olefinic terminal groups

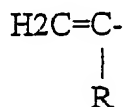
The invention concerns aromatic polyethers with olefinic polymerisable terminal groups.

Aromatic polyethers with olefinic groups are described, for instance, in DE-OS 29 17 819 (US-PS 4 207 406). Here, it is a matter of, e.g., copolymer of 2,6-dimethylphenol and 2-allyl-6-methyl-phenol. If one tries to polymerise copolymer of that type with other copolymerisable monomers, then weakly cross-linked insoluble products are formed, whose further processing is difficult.

Besides, acyl-coupled polymers of quinone coupled polyphenylene oxides are well-known, which can contain, among others, the maleic acid as acyl component (DE-OS 28 22 859, US-PS 4 156 772). But these polyphenylene oxides coupled with maleic acid, e.g., are not suitable for copolymerising with other monomers containing double bonds, so that they do not come into consideration as copolymerisation components.

The principle task of the present invention is to produce aromatic polyethers with olefinic, polymerisable terminal groups:

The task is accomplished according to the invention through aromatic polyethers, which contain an olefinic terminal group of the general formula



in which R can be hydrogen or an aliphatic alkyl group.

Hence, polyphenylene ethers of the patent claim 1 are the result of the invention.

A further result of the invention is the use of the polyphenylene ethers containing olefinic terminal groups as per claim 1 for the preparation of copolymers with other compounds containing polymerisable double bonds.

By aromatic polyethers are to be understood polyphenylene oxides, in which the ether-oxygen of a unit is bound to the aromatic ring of the neighbouring unit. Compounds based on polyphenylene oxides substituted in ortho position are preferable for polyethers. Besides, minimum 20 units should be linked with each other. The polyethers can carry in the ortho position the oxyhydrogen, halogen, hydrocarbon, halogenated hydrocarbon, phenyl groups and hydrocarbon-oxi-groups. Thus the following come into consideration : poly(2,6-dichloro-1,4-phenylene)-ether, poly(2,6-diphenyl-1,4-phenylene)ether, poly(2,6-dimethyl-1,4-phenylene)ether, poly(2,6-dibromo-1,4-phenylene)ether. These type of ethers have free phenolic hydroxyl terminal groups.

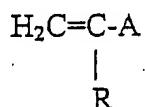
The aromatic polyethers are prepared, among others, by self-condensation of the corresponding monovalent phenols by the action of oxygen in the presence of a catalytic system, as described, for instance, in US-PS 3 219 625, 3 306 874, 3 306 875, 3 956 442, 3 965 069, 3 972 851.

It is a matter of a vinylic or allylic grouping in case of the olefinic polymerisable terminal groups. Vinylic terminal groups are preferred.

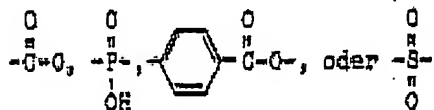
The production of the aromatic polyether with olefinic terminal group takes place, among others, by the conversion of the free phenolic hydroxyl terminal group with a compound, which contains a vinylic terminal group and a compound reacting with the hydroxyl terminal group of the aromatic polyether, leading to a linking of polyether and vinylic terminal group. For instance, acid halide, -anhydride or -ester, epoxide and isocyanate containing an olefinic double bond come into consideration. For

example, the following come into consideration: acrylic acid chloride, methacrylic acid chloride, methacrylic acid anhydride, p-vinyl-benzoylchloride, vinyl phosphonic acid dichloride, vinyl sulphonic acid chloride, vinyl isocyanate, vinyl chlorides. Besides, methylacrylic acid chloride, vinyl phosphonic acid dichloride and vinyl phosphonic acid chloride are preferred.

Preferred are polyphenylene ethers, which contain an olefinic terminal group of the general formula



in which R has the meaning indicated above and A can be following grouping:



The conversion of the aromatic polyether with these compounds occurs preferably in organic solvents as is, for instance, described in the publication "The chemistry of the hydroxyl group Part 1 p. 453 to 503 (1971) Interscience publishers London - New York - Sydney - Toronto - by S. Patai. Besides, the reaction can take place in the presence of catalysts like tert-amine or so-called "Phase-transfer-catalysts" like quaternary ammonium-, phosphonium-, arsenium- and tertiary sulphonium compounds.

The aromatic polyethers as per the invention can, e.g., be used as components for mixtures with other polymers like polystyrene, ABS. Especially, the polyethers can be copolymerised with other polymerisable compounds containing double bond like, for example, styrene, acrylonitrile, methacrylic acid methylester, alkyl-ester of acrylic acid, butadiene, isoprene. But, terpolymers can also be produced, which are formed from the aromatic polyethers with olefinic double bond and two additional compounds containing double bonds like, for example, styrene/acrylonitrile, styrene/maleinic acid anhydride, styrene/butadiene, acrylonitrile/butadiene. Such

copolymers are suitable, e.g., as thermoplastic plastic materials or for flameproof finish of thermoplastic plastic materials in combination with compounds containing phosphon/phosphonite.

The invention is explained with the help of following examples. The proportions indicated in the examples refer to the weight unless indicated otherwise.

Example 1

122 g poly(2,6-dimethyl-1,4-phenylene)ether, which was prepared by the conversion of 2,6-dimethylphenol in toluene in the presence of Cu-I-Br / dibutylamine and oxygen, is dissolved in 1100 g toluene at 80° C with intrinsic viscosity of 0.48 dl / g (measured at 30° C in chloroform). After cooling to 23° C, 55 g dimethylformamide and 22 g triethylamine are added. 160 g vinylphosphonic acid dichloride is added to that drop by drop with vigorous stirring and under nitrogen at 23° C. After the addition of the vinylphosphonic acid dichloride, it is stirred for another 2 hours at this temperature. Subsequent one more hour is allowed for subsequent reaction at 80° C, cooled down to room temperature and precipitated in 5500 g methanol. After thorough washing with methanol or water, is dried in vacuum at 1 Torr at 50° C. The product obtained after precipitation is 0.25 % by weight P and 0.01 double bonds/100 g polymer (iodometric titration after addition of ICl_3).

Example 2

100 g poly(2,6-dimethyl-1,4-phenylene)ether, which is got by the conversion of 2,6-dimethylphenol in toluene in the presence of Cu-I-Br / dibutylamine and oxygen and intrinsic viscosity of 0.32 dl / g (measured at 30° C in chloroform), is dissolved in 1000 g toluene at 80° C. After cooling to 50° C, 1 g of a 50 % aqueous sodium hydroxide solution and 0.01 g tetrabutylammoniumbromide are added to the solution under vigorous stirring. A solution of 1.1 g methacrylic acid chloride and 0.02 g di-tert.butyl-cresol in 10 ml toluene is added to it drop by drop in the course of 5

minutes at 50° C under vigorous stirring. After another 10 minutes, it is allowed to cool, neutralised with dilute acetic acid, precipitated in methanol, filtered out, washed with methanol and dried in vacuum at 1 Torr and 50° C. The product contains 0.015 double bonds/100 g polymer.

Example 3

The reaction is carried out analogous to example 2, except that, instead of methacrylic acid chloride, 6.3 g vinylsulphonic acid chloride is used. The product contains 0.3 % by weight S and 0.0094 double bonds/100 g polymer.

Example 4-9

Quantities of polyether, according to the invention, as indicated in table 1 from examples 1 to 3 are dissolved in the quantities of co-monomers indicated in table 1 and balance 20 parts by weight of ethylbenzene and polymerised at 140° C for 12 h in a high-pressure glass ampoule (bomb tube/Carius tube) sealed off under nitrogen. The polymer obtained is freed from the solvent and the remaining monomers at 50 ° C under vacuum. The composition is determined by IR-spectroscopy (styrene) and with the help of elemental analysis (acrylic nitrile). The intrinsic viscosity was measured at 30 ° C in chloroform.

The characteristic data are summarised in table 1.

Table 1

Example	Monomer composition		Copolymer composition		Intrinsic viscosity
	Polyether (% by wt.)	Comonomer (% by wt.)	Ethylbenzene (% by wt.)	Styrene Acrylonitrile [% by weight]	
4	Example 1 (8)	Styrol (54) Acrylnitril (18)	(20)	68 20	0.53
5	Example 1 (24)				
6	Example 1 (40)				
7	Example 2 (40)				
8	Example 3 (40)				